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The Raman Spectra of Iodides, Part I, Phosphonium Iodide and Methyl Iodide.

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Abstract.

The Raman effect in *crystals of phosphonium iodide* has been studied with a view to correlate it with the crystal structure of the compound. The frequencies found are 930 (2), 1040 (0), 1113 (0), 1259 (1), 1416 (1), 2304 (10), 2370 (8). All these frequencies are attributed to the ionic group PH_4 found in the crystal which is assumed to be distorted under the influence of the neighbouring iodine ions.

The Raman spectrum of methyl iodide liquid has been studied thoroughly, the method of continuous distillation[1] being used to avoid the effect of photo-chemical decompositon. The following thirteen frequencies, of which five are being reported for the first time have been established :—

524 (8), 895 (1), 1028 (0), 1242 (3), 1434 (1), 1760 (0), 2050 (0), 2461 (1), 2557 (1), 2796 (1), 2849 (1), 2950 (5), and 3050 (3).

Allowing for the small diminution of frequency which occurs in passing from the vapour to the liquid state, every one of the Q branches observed in the infra-red absorption of the vapour by Bennet and Meyer[2] has a corresponding Raman line.

[1] N. N. Pal and P. N. Sengupta, Ind. J. Phys., 5, 609 (1930).

[2] Willard H. Bennet and Charles F. Meyer, Phys. Rev., 32, 888 (1998).

1. *Phosphonium Iodide.*

Crystals of phosphonium iodide supplied by Kahlbaum in sealed tubes were used. They were of fairly large size and had a faint yellow tint though they were of 'pure' quality. One of the unopened tubes was used in the experiment. Light from a mercury lamp was focussed by a powerful condenser on the centre of the tube and the scattered light examined by a Fuess glass spectrograph of high dispersion. On using Ilford Isozenith plates (speed No. 700 H & D), which were backed before use, it was found that 48 hours of exposure was enough to bring out all the lines including the weaker ones. The plates were measured on a Hilger micrometer and the wave-length of the lines were calculated by using the simplified form of Hartman's interpolation formula, with the known mercury lines as standards. The wave numbers (in vac. per cm.) were calculated and the shifts in wave numbers of the Raman lines from the corresponding exciting lines determined. The following table represents the results of the analysis. The exciting lines are 4046·6 and 4358·3 and are represented by the letters *d* and *h* respectively.

TABLE I.

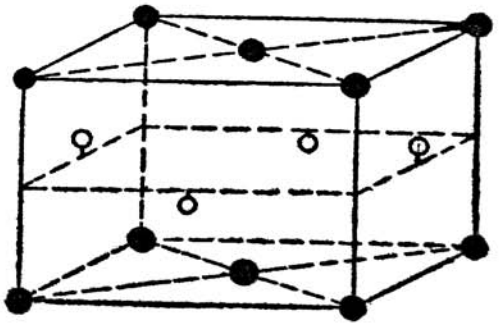
I.	ν.	$\Delta\nu$.	Remarks.
10	22401	*d*—2304	Sharp, strong
8	22338	*d*—2367	Diffuse
2	22008	*h*—930	Sharp, faint
0	21893	*h*—1040	Faint
0	21825	*h*—1113	Faint
1	21679	*h*—1259	Diffuse
1	21522	*h*—1416	Diffuse
10	20634	*h*—2304	Sharp, strong
8	20568	*h*—2370	Diffuse

$\Delta\nu$=930 (2), 1040 (0), 1113 (0), 1259 (1), 1416 (1), 2304 (10), 2370 (8).

Another exposure was given only for 12 hours with a fairly strong aqueous solution of quinine sulphate on the path of the incident rays which diminished the intensity of the Raman lines arising from 4046·6. The results thus obtained confirmed the assignments shown in Table I.

2. *Discussion.*

Crystals of phosphonium iodide are cube-like in appearance, but have been shown to be tetragonal and the cube-like habit has been attributed to combination of (110) and (001). The study of crystal structure of this compound by Dickinson[3] revealed that the arrangement of the phosphorous and iodine atom is as shown in the figure where the black circles represent the phosphorous atoms and the white circles represent the iodine atoms. As a result of a small displacement of the iodine atom from the exact centre, each phosphorous atom instead of having 8 iodine atoms equidistant from it, has four, at a distance which is different from the distance of the remaining four. In so far as no grouping of the phosphorous and iodine atoms could be made, the structure has been considered ionic.



As is well known, the distinct difference between the ionic and molecular lattice finds a counterpart in the Raman

[3] Roscoe, G. Dickinson—J. Ann. Chem. Soc., XLIV, 1489 (1922).

spectra. While typical molecular crystals show the Raman lines very prominently, ionic crystals such as NaCl give no lines or only extremely faint lines which are in fact so weak that their appearance is explained as due to a second order effect namely the lattice of sodium ions oscillating against the lattice of chlorine ions. From the X-ray investigations, PH_4I has to be considered an ionic crystal and may be expected to exhibit in scattering only the lines due to the internal oscillations within the ion PH_4. We cannot, under the experimental conditions described, expect such a weak effect as the lattice oscillation to manifest itself distinctly. Secondly the lattice oscillations due to such massive and ionic system as the phosphonium *ion* and the iodine *ion* should be of fairly low frequency (as could be easily seen by a comparative study) of the order of 100 wave numbers. In the results obtained, there is no line of such low frequency. The data from scattering thus appears to be consistent with the structure of the crystal inferred from X-ray measurements.

It would be of interest to compare the data with the infra-red data available in the case of phosphine. This was thoroughly studied by Robertson and Fox[4] who assigned 676·7, 993.2 and 1125 as the fundamental frequencies. Badger and Mecke[5] after a critical study of the results and comparing it with the results deduced in the case of ammonia, concluded that the fundamentals of PH_3 are $\gamma_1 = 2327$; $\gamma_2 = 1125$ and $\gamma_3 = 993 \cdot 2$. It is very probable however that there is also a fourth fundamental which has been overlooked in the analysis. The appearance of the two lines 2304 and 2370 in the scattering by phosphonium iodide confirms the view that PH_3 possesses at least one fundamental frequency in the vicinity of these lines. Accepting this view, we have a rough correspondence between the Raman frequencies for PH_4I and the

[4] R. Robertson and J. J. Fox, Proc. Roy. Soc., A. Vol. 120, p. 128 (1928).
[5] R. M. Badger and R. Mecke, Zeits. f. Phys. Chem., 5, Abt. B, p. 333 (1929).

infra-red fundamentals of PH_3. The values for PH_4I (Table II) are slightly less than the corresponding values for PH_3. This result is analogous to the shifts[6] of frequency observed in passing from SO_3 to SO_4 (Table III).

TABLE II.

Infra-red data for PH_3 gas.	Scattering for $[PH_4]I$ solid.	Dif.
993	930	63
	1040	...
1125	1113	12
...	1259	...
...	1416	...
2327	2304	23
...	2370	...

TABLE III.

SO_3	SO_4	Dif.
534	450	84
...	614	...
1068	989	79
1403	1218	185

In the case of the four frequencies, 1040, 1259, 1416 and 2370 of PH_4I, there is no corresponding value in the infra-red data for PH_3.

Accepting the view that all the lines recorded for PH_4I, are due to the ion (PH_4^+) we may divide them into four groups, namely, 930, the weak pair 1040 and 1113, the strong pair 1259 and 1416 and the very strong pair 2304 and 2370. The 930 line stands by itself being the sharpest of all, but of low intensity. The pair 1040 and 1113 are both very weak and diffuse and in fact might easily be overlooked on the plate except on a careful examination. The pair 1215 and 1416 are of identical appearance and intensity. The pair 2304 and 2370 similar in possessing great intensity, differ

[6] S. Bhagavantam, Ind. Jour. Phys., 5, 93 (1930).

in the fact that 2304 is sharp while 2370 is diffuse, the former being more intense. This natural division has one point against it, in so far as it does not, according to the well-known facts isolate the single intense and sharp line which is attributed to the symmetrical expansion and contraction of the tetrahedron.

If the configuration of the (PH_4^+) group be a perfect tetrahedron, it would have four fundamental frequencies. A distorted tetrahedron would have nine fundamental frequencies which could be grouped by comparison with the case in which the distortion vanishes as 2 (doublet) 3 (triplet) 1 single and 3 (triplet) forming nine lines in all.

The structure obtained by placing in a unit of dimensions $6{\cdot}34 \times 6{\cdot}34 \times 4{\cdot}62$ Å, phosphorous atoms at (000) and $(\frac{1}{2}, \frac{1}{2}, 0)$ and the iodine atoms at $(0, \frac{1}{2}, u)$ and $(\frac{1}{2}, 0, \bar{u})$ where u is close to 0·40 is observed to explain the X-ray data of this compound satisfactorily. Consistent with the symmetry of the phosphonium iodide arrangement, the hydrogen atoms also may be grouped round the phosphorous atom to occupy the equivalent positions (corresponding to the space group, D_{4h}^{7}).

$(uov)\ (\bar{u}\,ov)\ (o\bar{u}v)\ (ou\bar{v}),\ (\frac{1}{2}+u, \frac{1}{2}, v)\ (\frac{1}{2}-u, \frac{1}{2}, \bar{v})\ (\frac{1}{2}, \frac{1}{2}+u, v)$
$(\frac{1}{2}, \frac{1}{2}-u, v),$

where u and v may have values from 0 to 1. If the exact value of u and v is known, the shape of the tetrahedron is determined. Because of the low mass of hydrogen atoms, X-ray data fail to give any information about this. It is possible to attribute such values to u and v and make the resulting tetrahedron a regular one, but the probability is that the tetrahedron is a distorted one. This appears to be more correct if the nature of arrangement of the iodine atoms round the phosphorous atom is considered. Since the iodine atoms are arranged round any phosphorous atom not as a group of eight, but as two groups of four, the distortion of the (PH_4)

under these different forces is inevitable. The frequencies obtained may accordingly be classified as

$$\left.\begin{matrix} 930 \\ 1040 \end{matrix}\right\} \quad \left.\begin{matrix} 1113 \\ 1259 \\ 1416 \end{matrix}\right\} \quad 2304 \text{ and } 2370.$$

The 2370 frequency may be a close triplet which is not sufficiently well resolved and is seen to be a single line. Another possible explanation is to assume that the tetrahedron is distorted only to that extent to produce only these 7 frequencies.

A study of the polarisation of lines in a solution of phosphonium iodide in a suitable solvent will show which of these two is the correct assignment.

The symmetrical expansion and contraction of the tetrahedron causes the 2304 frequency. Compared with the results obtained from other similar compounds as methane, the tetrachlorides of carbon, silicon, tin, etc.,[7] this assignment appears to be justifiable. Thus in the case of CCl_4 of the four frequencies,

$$217, \quad 313, \quad 459 \quad \left\{\begin{matrix} 760 \\ 791 \end{matrix}\right\}$$

the Raman frequency of 459 has properties identical with those of the line under consideration and this has been attributed to a similar type of oscillation. The most recent results obtained by Bhagavantam[8] with another similar hydride—methane—are seen to confirm this view. Frequencies 1304, 1520, 2918, 3018 are taken as the fundamentals of this molecule and the line 2918 singled out from others because of its

[7] Bhagavantam—*Loc. cit.*

[8] S. Bhagavantam—Ind. Jour. Phys. VI, 595 (1932).

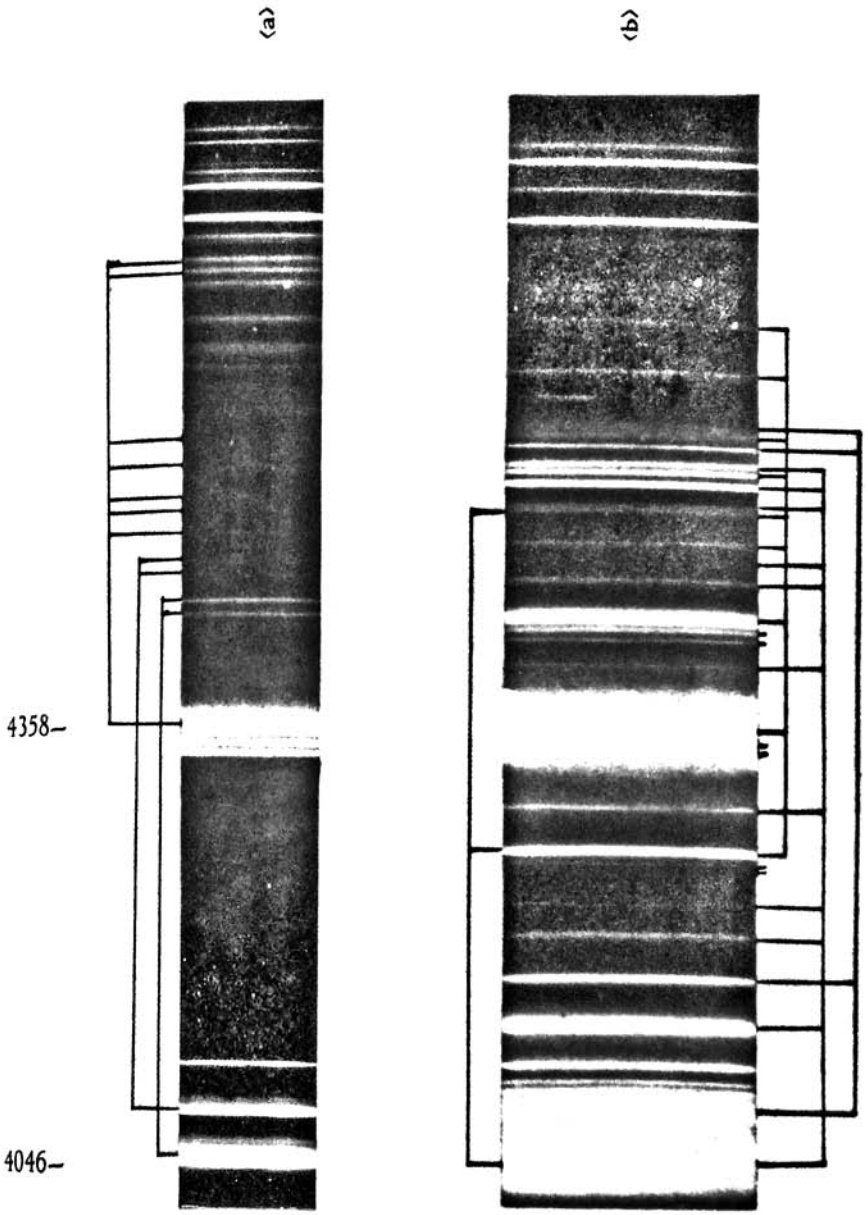
sharpness and intensity. This too has been ascribed to a symmetrical expansion and contraction of the tetrahedron.

The remaining lines may be identified with the other three modes of vibration of a tetrahedron. Thus, the line at 2370 and $\begin{Bmatrix}1113\\1259\\1416\end{Bmatrix}$ can be ascribed to the two different modes in which the central atom moves within the tetrahedron. The $\begin{Bmatrix}930\\1040\end{Bmatrix}$ frequency may correspond to one in which the hydrogen atoms move about transversely.

3. *Methyl Iodide.*

The procedure recommended by Pal and Sengupta[9] is used here. As a result of the continuous distillation that is made to go on during the exposure, the photochemical decomposition which causes the liquid to become brownish or yellow is prevented and the plate obtained is free from continuous spectrum. An exposure of 24 hours brought out all the strong lines. The plate showed indications of the presence of certain feeble lines, and accordingly, a long exposure of 120 hours was given to bring out these strongly. Golden Isozenith plate, (speed 1400 H & D) was used and was backed before use. The experimental procedure for the measurement of the plate is the same as for phosphonium iodide. The following table gives the result of analysis. The intensities of the Raman lines (I) their wave-numbers (ν) and the shifts in wave numbers ($\triangle\nu$) are given under the respective columns. The incident exciting lines 3650·1; 3654·8; 3663·3; 4046·6; 4077·8; 4339·5; 4347·5 and 4358·3 are represented by the letters, *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h* respectively.

[9] Pal and Sengupta—*Loc. cit.*



(a) Phosphonium iodide, (b) Methyl iodide.

Raman Spectra.

TABLE IV.

I.	Wave No. ν.	$\Delta\nu$.	I	Wave No. ν.	$\Delta\nu$.
2	25229	d + 524	1	22472	g − 523
0	25040	c + 524	8	22416	h − 522
3	24440	a −2049	1	22244	d −2461
3	24404	b −2950	1	22148	d −2557
0	24241	b −3049	1	22042	h − 896
8	24181	d − 524	1	21909	d −2796
4	23991	c − 525			h −1029
1	23811	d − 894	1	21856	d −2849
0	23678	d −1027	5	21755	d −2950
1	23566	f + 527	3	21698	h −1240
1	23518	g + 523	3	21654	d −3051
5	23461	h + 523	3	21566	e −2950
		d −1244	1	21506	h −1436
1	23272	d −1433	1	21460	e −3056
0	22655	d −2050	0	21178	h −1760
1	22516	f − 523	0	20887	h −2051

$\Delta\nu$ = 524 (8); 895 (1); 1028 (0); 1242 (3); 1434 (1); 1760 (0); 2050 (0); 2461 (1); 2557 (1); 2796 (1); 2849 (1); 2950 (5); 3050 (3).

To help the identification of various lines, an exposure for 120 hours with a ortho-cresolphthalein filter on the path of the incident rays was taken in which, it was seen that the lines due to 4046 were weakened considerably or were completely cut out. Besides diminishing the intensity of 4046, this filter wipes out the faint mercury bands present in the neighbourhood of 4797 A.U. thereby helping us to detect any Raman line that may be present in this region.

4. *Discussion.*

The Raman spectra of this compound has been investigated by various workers including Dadieu-Kohlrausch,[10] Ball,[11] Cleeton and Dufford.[12] A comparison of the results of the various investigators is included along with the infra-red frequency data available. Coblentz[13] studied the infra-red absorption spectra of methyl iodide in the liquid state while Bennett and Meyer investigated the vapour up to 14 μ. Recently, Sleator[14] investigated the infra-red absorption data of the compound in vapour state, beyond this region—up to :0 μ approximately and observed a new band at 18·78 μ. The results obtained are in fair agreement. Only the Q branch of the band is referred to, neglecting the fine structure of the band.

A comparison of the Raman spectra of the substance with the infra-red data reveals certain interesting details.

The infra-red absorption data for vapour are taken from Bennett and Meyer's tables excepting 532 which is from Sleator's work. The infra-red absorption data for liquid is from Coblentz's "Investigations of Infra-red spectra."

The varous frequencies recorded, correspond to various modes of oscillation of the molecule. These modes of oscillation may be divided into two types: those in which the electric moment vibrates parallel to the axis of symmetry of the molecule, and the second type, in which the vibration of the electric moment is perpendicular to the axis of symmetry. The former produces the band of the $\|^1$ type and the latter is responsible for the band of the $\perp^r$ type. The frequencies at

[10] A. Dadieu & K.W.F. Kohlrausch, Wien. Ber. *139*, 77 (1930).
Do. Wien. Ber. *139*, 717 (1930).
[11] G. N. Ball, Z. f. Phys., *66*, 257, (1930).
[12] C. D. Cleeton & R. T. Dafford, Phys. Rev., *37*, 362 (1931).
[13] Coblentz, "Investigations of Infra-red spectra."
[14] W. W. Sleator, Phys. Rev., *38*, 147, (1931).

TABLE V.

Ball.	Cleeton-Dufford.	Dadieu-Kohlrausch.	Pai.	Infra-red frequency.	
				Vapour.	Liquid.
509	534	522	524	532 ∥'	
					668
					717
					813
			895	885 ⊥	885
					985
			1028		1026
					1087
1248	1254	1239	1242	1252 ∥'	1217
		1416	1434	1446 ⊥'	1408
			1760		1695
					1852
			2050		
					2174
			2461		
	2589		2557		
	2771		2796		
		2889	2849	2861 ∥'	
2953	2946	2947	2950	2970 ∥'	2940
	3036	3046	3050	3074 ⊥'	

2950, 2849, 1242 and 524 belong to the first type while those at 3050, 1434 and 895 represent the second type. These three frequencies 3050, 1434 and 895 appear in descending order of intensity in scattering, the 895 being a very weak line. In the infra-red however, this happens to be the most intense

absorption band, the 1434 coming second in order of magnitude, and the 3050 being feeble. In the case of the four frequencies classed under the first type, there is no such order to be noticed. In the first place, there is the 1242 frequency, which has manifested strongly in the infra-red absorption while in scattering also, it has come out as a fairly strong line. In the case of the 524 line, it appears as an intense line in scattering, while in the infra-red it is only a feeble band.

As a contrast to this type of frequency, there are two sharp lines at 1028 and 2050 which are weak both in scattering and in the infra-red absorption.

The remaining four frequencies, 1760, 2461, 2557 and 2796 have no correspondence with the infra-red absorption data. They all appear as diffuse and feeble lines.

Just as there is a good correspondence between the infra-red absorption data for the monohalogen substituted derivatives of methane, the correspondence is found to be present in the scattering also. The following table shows the result at a glance.

A critical study of this table reveals that the Raman data in all these cases except for methyl iodide are very incomplete. A thorough investigation in the case of the other halides is sure to throw more light on the subject.

The author's best thanks are due to Prof. Sir C. V. Raman at whose suggestion the work was taken up, for his keen interest and kind guidance.

TABLE VI.

Methane.		Methyl fluoride.		Methyl chloride.		Methyl bromide.		Methyl iodide.	
Scattering.	Infra-red. gas.	Scattering.	Infra-red vapour.	Scattering in liquid.	Infra-red vapour.	Scattering in liquid.	Infra-red vapour.	Scattering in liquid.	Infra red vapour.
	1304		1049	712	732	594	615	524	532
			1200	1098	1019		957	895	885
								1028	
			1476		1355	1296	1306	1242	1252
	1520				1460		1451	1434	1446
								1760	
								2050	
								2461	
								2557	
								2796	
			2862	2815	2880		(2862)	2849	2861
2918			2965	2955	2967	2956	(2978)	2950	2971
3018	3013		2987	3024	3047	3050	3062	3060	3074